Assessment of Metals in Massachusetts Municipal Wastewater Treatment Facilities

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ABSTRACT

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In an attempt to assess the removal of metals in wastewater treatment plants and also to evaluate the potential toxicity of effluents, an extensive sampling program was conducted at 27 Massachusetts municipal wastewater treatment facilities. Influents and effluents were analyzed for selected metals. No relationship was found between effluent and influent concentrations, nor between removal of metals and removal of solids. In addition, estimates of toxicity based on the concentrations of the metals varied widely among effluents and in the same effluent over time. The metals monitored were Al, Cr, Fe, Mn, Ni, Ag, Cu, Pb, and Hg, and the last three of these amounted for over 90% of the calculated toxicity of the samples.

Publication # 16670-22-50-9-88-C.R.
Approved by Ric Murphy, State Purchasing Agent

ASSESSMENT OF METALS IN MASSACHUSETTS MUNICIPAL WASTEWATER TREATMENT FACILITIES

Nora Hanley and Russell A. Isaac

Introduction

Concern about toxic substances in wastewater has increased over the last several years. As part of its efforts to assess the problem, the Massachusetts Division of Water Pollution Control conducted a survey of the concentration of selected metals in the influents and effluents of public wastewater treatment facilities (WWTF's) in Massachusetts.[1] The objectives of the effort were to:

1) Inventory influent concentrations

2) Inventory effluent concentrations

3 Assess removals by individual unit processes

4 Compare plant types based on removal efficiencies

5) Assess potential toxicity associated with the metals that were measured in effluents.

Methods

Twenty-seven wastewater treatment facilities (Figure 1) were classified into three major categories based on the treatment provided as presented in Table I. Secondary plants were differentiated further into three categories making a total of five classifications. Samples generally were 24-hour composites and were analyzed for total* metals at the Lawrence Experiment Station by flame atomic absorption spectrophotometry for all parameters except mercury which was measured using the cold vapor spectrophotometric procedure. In addition, samples were analyzed for conventional parameters which included suspended solids, BOD_5, total phosphorus, Kjeldahl-N, NH_3-N, NO_3-N.

Results

a) Overall Removal of Metals

The concentrations of metals in the influents were evaluated as a single data set to characterize what is entering treatment plants. The median concentration of each metal measured in the influents is below the corresponding national median as summarized in Table II.

The substantial removal of metals is reflected in the median concentrations in the effluents being lower than those in the influents for all parameters except cadmium (Table II). The median concentration of cadmium was below detection limits for both influents and effluents.

Wastewater treatment plants were divided into five categories: primary, activated sludge, extended aeration, trickling filter and tertiary. The ter-

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* i.e. dissolved and particulate were not differentiated

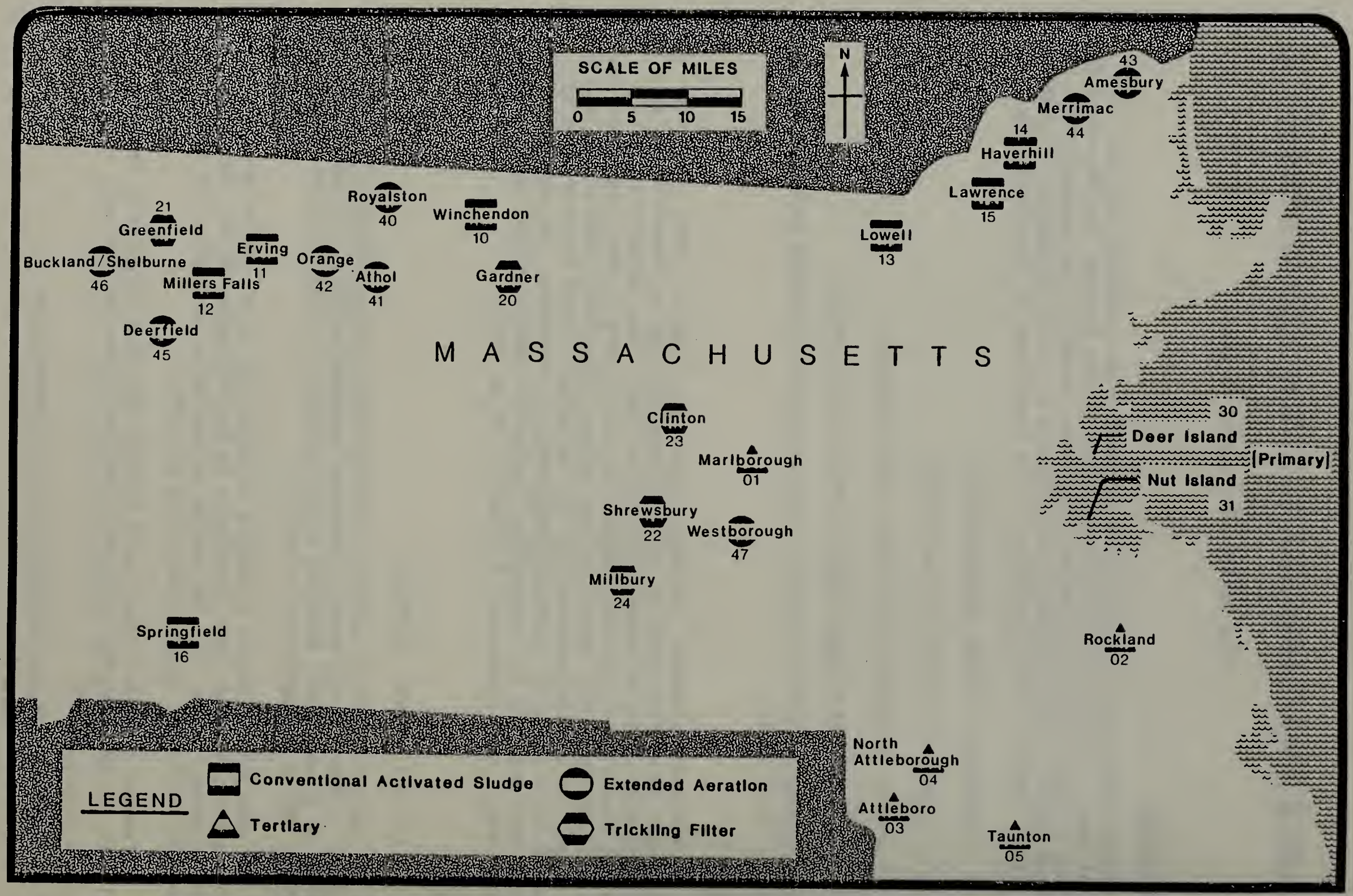

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Figure 1

TREATMENT PLANT LOCATION, TYPE, AND NUMBER

TABLE I

WASTEWATER TREATMENT PLANT CATEGORIES

1.	Primary	2
2.	Secondary	
	a. conventional activated sludge	7
	b. extended aeration	8
	c. trickling filter	5
3.	Advanced*	5

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* Includes plants employing nitrification or filtration of final effluent

TABLE II

INFLUENT AND EFFLUENT METALS CONCENTRATIONS FOR 27 WWTF's

IN MASSACHUSETTS* COMPARED TO NATIONAL SURVEY

	INFLUENT CONCENTRATION, µg/l				EFFLUENT CONCENTRATION, µg/l		
METAL	RANGE	MEAN	MEDIAN	MEDIAN (NATIONAL DATA)**	RANGE	MEAN	MEDIAN
Aluminum	0-13,000	1308	865	3390	0-1,600	320	200
Cadmium	0-210	17.9	0	24	0-110	7	0
Chromium	0-1,600	116	30	400	0-320	21	10
Copper	40-9,800	673	230	420	0-490	116	65
Iron	210-23,000	2,280	1,600	3,180	0-5,400	603	290
Mercury	0-6.00	0.68	0.40	0.596 (est)	0-1.70	.23	.10
Manganese	30-2,300	268	170	--	0-850	115	95
Nickel	0-860	60	20	230	0-270	31	0
Lead	0-1,300	107	70	120	0-320	46	40
Zinc	50-3,400	312	200	520	10-330	111	90
Silver	0-900	27	10	10 (est)	0-100	6	0

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* Approximately 68 composite samples
**Reference 2

tiary category includes plants which provide advanced biological treatment (nitrification) as well as those that provide sand filtration of the secondary effluent. Tertiary, activated sludge, and extended aeration plants performed similarly for most metals (Figures 2a and 2b). However, statistical analysis of the data indicate that tertiary plants' mean removals of Mn, Zn, Al, Fe, Cu, and Hg are higher than the mean removals in extended aeration plants with a probability equal to or exceeding 90% as summarized in Table III. Similar findings except for Cu result from employing the non-parametric Krushal-Wallis test for the same group of elements. Data were too variable to draw conclusions for trickling filters.

Thus, overall, the tertiary and conventional activated sludge plants were the most efficient in removing metals. Except for manganese and cadmium, removals exceeded 50% and were close for both treatment schemes (Figure 2a and 2b).

b) Removals by Unit Processes

A unit process can be defined as a discrete chemical or biological operation. Within WWTF's, the unit operations of interest are primary settling(1°), secondary treatment (biological/2°) and tertiary treatment(3°), which, in this paper, can be either nitrification or filtration.

In this study, in comparing 1°, 2° and 3° unit processes, secondary, or biological, treatment generally removes metals most effectively, followed by 1°, and then 3° unit processes, as shown in Figure 3. The fact that tertiary units are preceeded by biological units may influence these results since the first unit in a train may remove what is most amenable to treatment.

Evaluation of Removals

Various relationships among the data were evaluated in an attempt to better understand the dynamics of removal. The correlation of effluent concentrations with influent concentrations generally was weak. Only in the case of nickel did this correlation explain more than 50% of the variation in the data as summarized in Table IV. The correlation between the percentage of metals removed and the percentage of suspended solids removed was equally weak. Again, only for one element, in this case aluminum, was more than 50% of the variation in the metal's removal accounted for by the removal of suspended solids as presented in Table IV. It is possible that analyzing dissolved and particulate metals separately would reveal stronger correlations.

Calculations of removal efficiencies are markedly influenced by the precision of the laboratory analyses. Concentrations of elements near detection limits cause wide variations in estimates of removal efficiencies and may account for some of the negative removal values. Also, carryover of metals laden solids and release of metals from solids to the liquid stream could account for negative removals.

Evaluation of Metal Toxicity

In an effort to rank the potential toxicity of the effluents, the concentration of each element was divided by the appropriate water quality criterion, as listed in Table V, yielding what here is defined as the toxicity units for each element. These values or toxicity units were then

Figure 2a MEDIAN PERCENT REMOVAL BY PLANT TYPE:

MEASURED METALS

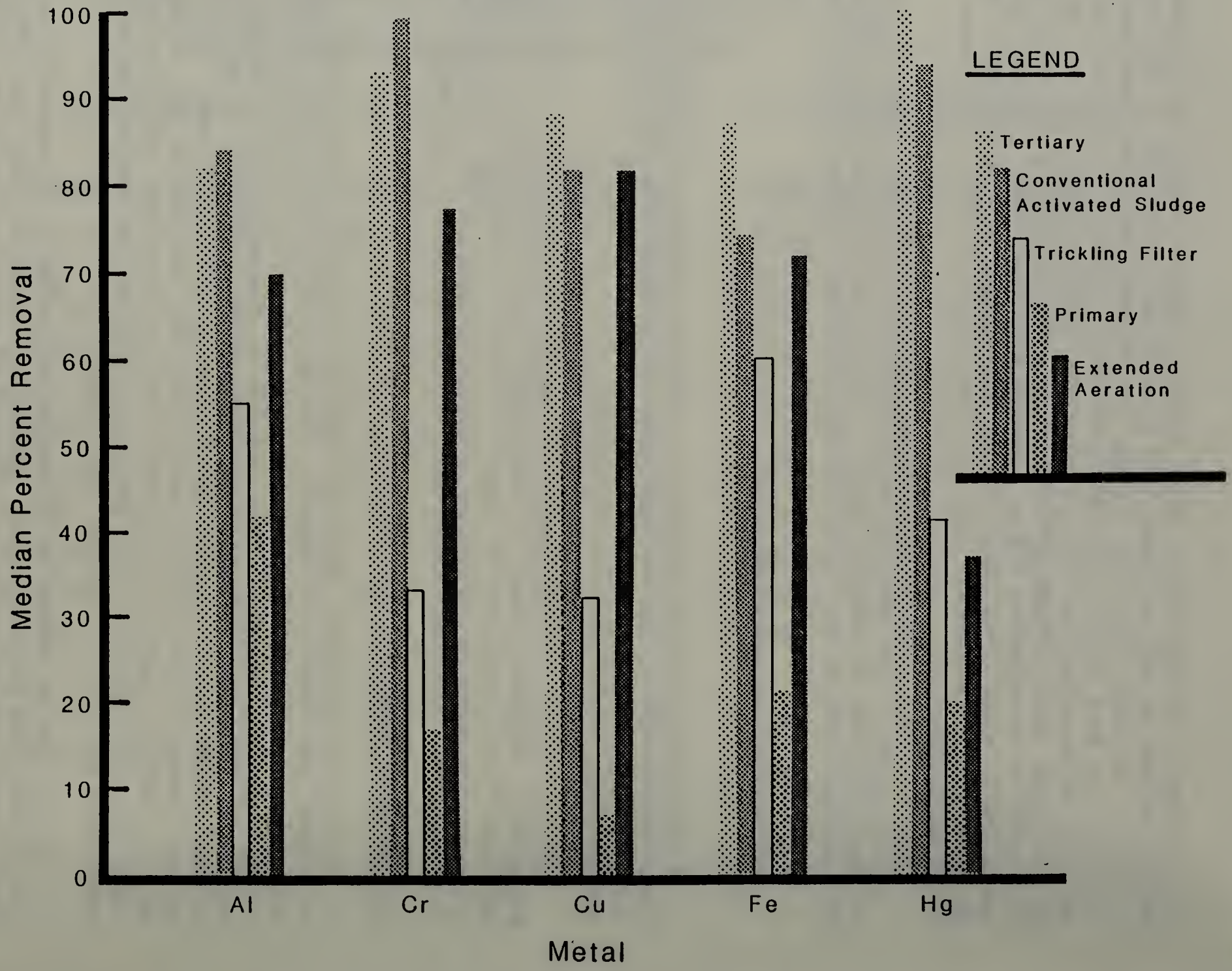

Figure 2b MEDIAN PERCENT REMOVAL BY PLANT TYPE :

MEASURED METALS

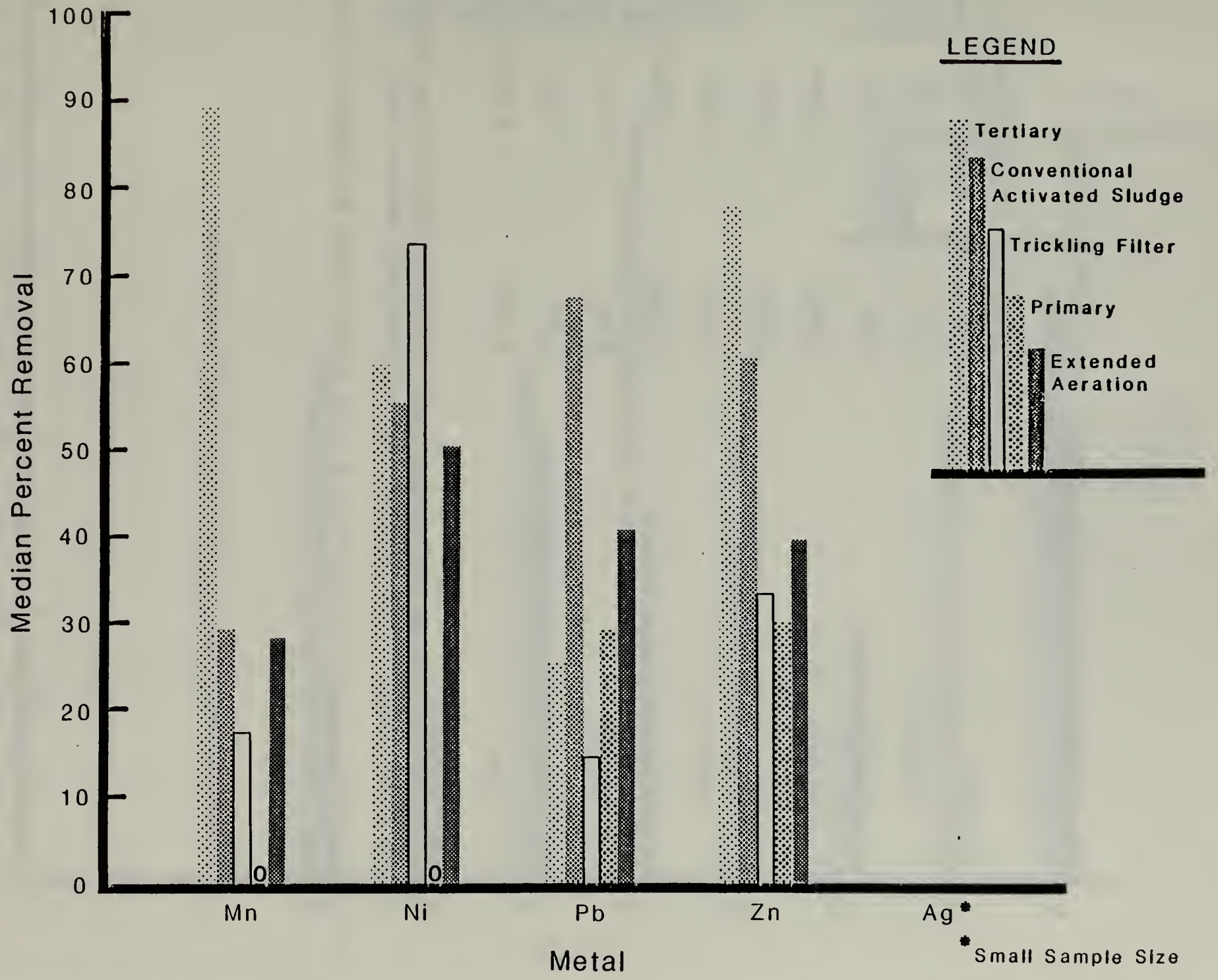

TABLE III

COMPARISON OF METALS REMOVAL IN EXTENDED AERATION AND TERTIARY WWTF's

	EXTENDED AERATION p	TERTIARY WWTF's (1-p)**
Aluminum	0.10	0.90
Chromium	0.26	0.74
Copper	0.046	0.954
Iron	0.070	0.930
Mercury	0.074	0.926
Manganese	0.0094	0.9906
Nickel	0.99	0.01
Lead	0.91	0.09
Zinc	0.0077	0.9923

* Probability that values for removal come from same distribution obtained using a two sample t-test, population variance not assumed equal

** Probability removals by tertiary plants exceed those by extended aeration plants

Figure 3 UNIT PROCESS EFFICIENCIES:

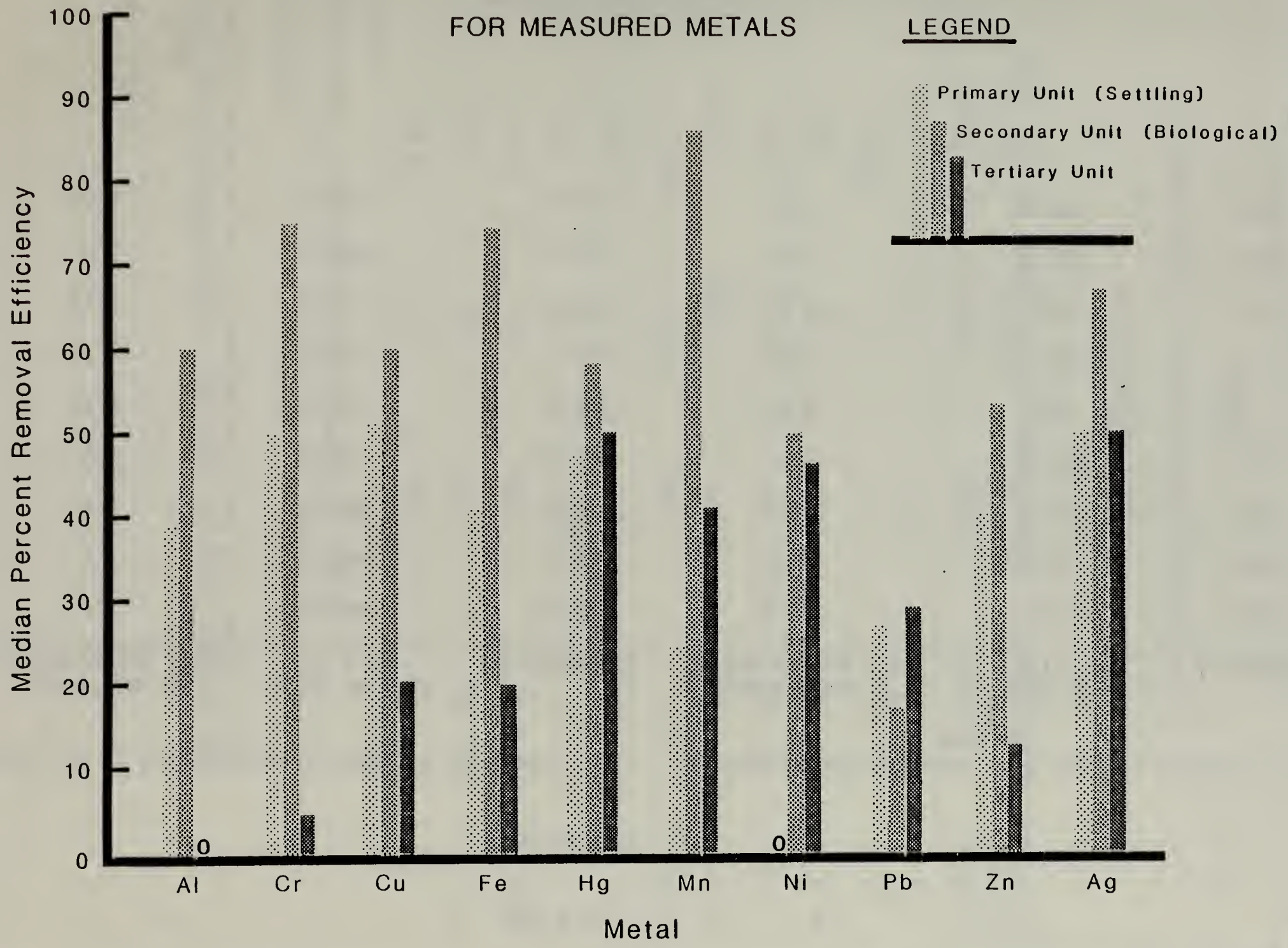

TABLE IV

CORRELATIONS

	Metals Concentration in Effluents with Those in Influents			Percent Metals Removals with Percent Suspended Solids Removal		
METAL	COEFFICIENT OF DETERMINATION X 100	SLOPE OF BEST FIT LINE	y-INTERCEPT	COEFFICIENT OF DETERMINATION X 100	SLOPE OF BEST FIT LINE	y-INTERCEPT
Aluminum	3.2	0.0244	24.0	61.6	1.10	28.6
Chromium	9.1	0.0486	1.01	34.4	1.28	42.8
Copper	6.9	0.0235	10.0	4.0	0.951	32.8
Iron	0.6	0.018	47.6	7.2	0.868	16.8
Mercury	25.5	0.153	0.964	11.6	2.08	137
Manganese	27.3	0.201	5.36	18.5	0.951	46.5
Nickel	63.0	0.327	1.07	4.6	0.682	23.1
Lead	0.6	0.0205	4.34	1.1	0.272	11.9
Zinc	10.4	0.051	8.53	20.3	0.847	25.6

TABLE V

CALCULATED TOXICITY ASSOCIATED WITH MEASURED METALS

MASSACHUSETTS WWTF's

METALS	WATER QUALITY CRITERION (µg/l)	CONCENTRATION MEDIAN (µg/l)	MEDIAN METAL TOXICITY UNITS+	CONCENTRATION MEDIAN (µg/l)	MEDIAN METAL TOXICITY UNITS+
Aluminum	100	865	8.65	200	2.0
Cadmium	0.66*	0	0	0	0
Chromium	120*	30	0.25	10	0.08
Copper	6.5*	230	35.4	65	10.0
Iron	1000	1600	1.6	290	0.29
Mercury	0.012*	0.40	33.3	0.10	8.33
Manganese	50**	170	3.4	95	1.90
Nickel	56	20	0.36	0	0
Lead	1.3*	70	53.8	40	30.77
Zinc	56++	200	3.6	90	1.61
Silver	0.82	10	12.2	0	0

+ Defined as median concentration/water quality criteria

++ 30-day average

* 4-day average value not to be exceeded more than once every 3 years. For 50 mg/l Alk where applicable. Fed. Reg. V50 N145 July 29, 1985 30784-30796

** For water supply

summed for each effluent sample to obtain an estimate of each effluent's toxicity associated with the measured metals. Thus, comparisons could be made between effluents based on each effluent sample's potential toxicity using the index just described. Major findings based on this analysis are:

1. The total influent and effluent toxicity values are consistent with a log normal distribution as illustrated by Figure 4.

2. The variation of the toxicity index with time for a particular effluent approximates the range found when comparing all the effluents together as revealed in Figure 5.

3. Single variate correlation analysis of the data indicated that 47% of the toxicity could be explained by lead, 35% by mercury and 24% by copper, respectively. Multiple regression analysis indicated these three parameters accounted for 90% of the total metals toxicity index as presented in Table VI.

4. Correlation between toxicity, as measured by toxicity units, in the effluents and that in the influents was essentially zero as depicted in Figure 6.

Conclusions

1. The concentration of the measured metals and thus the associated toxicity were highly variable in the effluents tested. Therefore, multiple samples are required to define the range of toxicity likely to be encountered in effluent.

2. Much of the toxicity associated with the measured metals in the effluents sampled could be accounted for by three parameters - Pb, Hg and Cu. For the effluents sampled, these three parameters would provide a good estimate of the toxicity associated with the suite of eight, thus, allowing a reduction in the number of individual analyses required to assess toxicity from total metals.

3. Essentially, no correlation existed between influent and effluent toxicity indices. This lack of correlation is not surprising given the low correlation between the influent and effluent concentrations of individual metals.

4. Substantial, albeit variable, removals of metals and their associated toxicity is accomplished in common wastewater treatment facilities. As might be expected, tertiary plants performed best but only slightly better than secondary plants using activated sludge.

5. The activated sludge process is the most efficient unit process in removing metals.

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Figure 4 DISTRIBUTION OF CALCULATED TOXICITY ASSOCIATED WITH MEASURED METALS : INFLUENT AND EFFLUENT

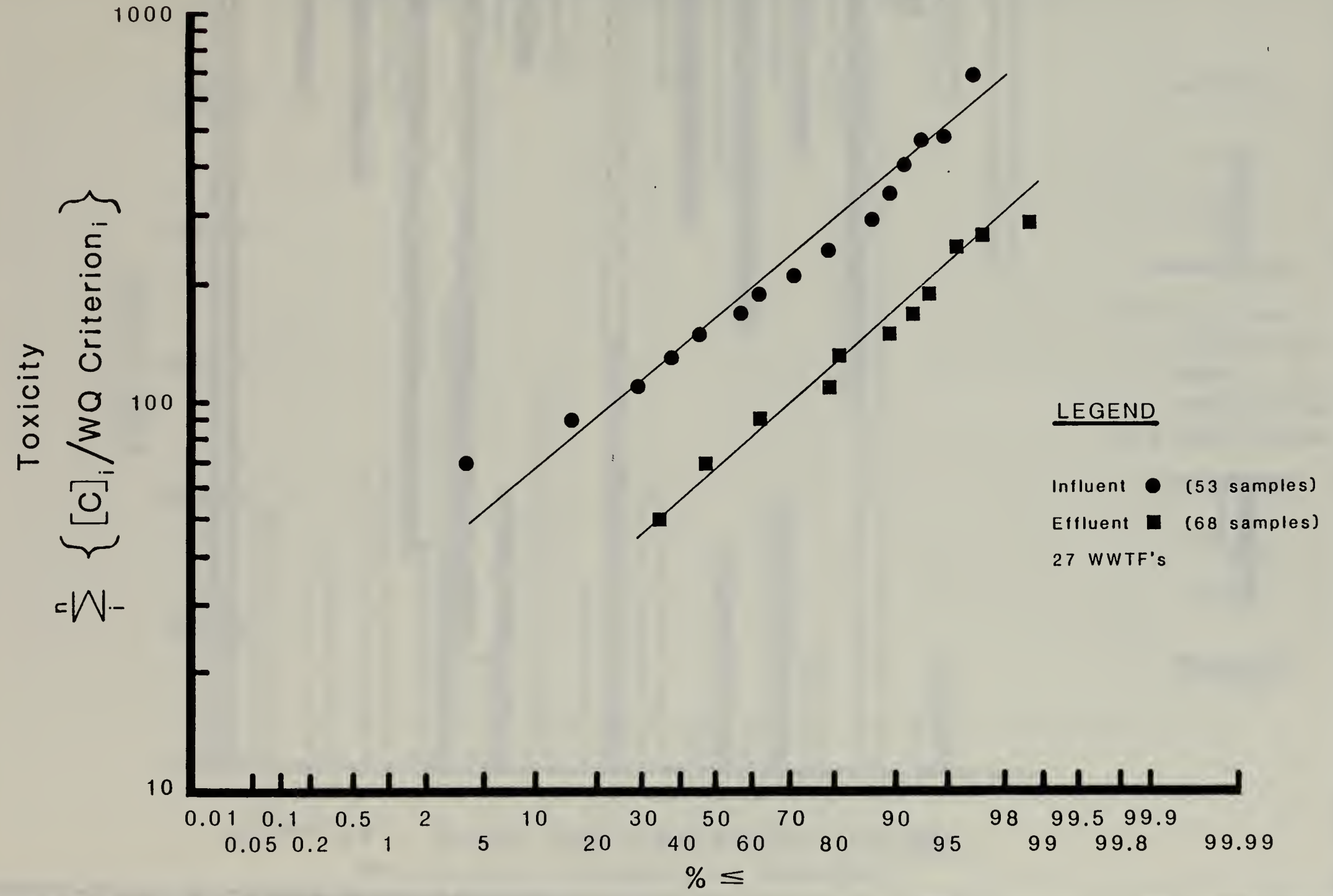


Figure 5a VARIATION IN EFFLUENT TOXICITY

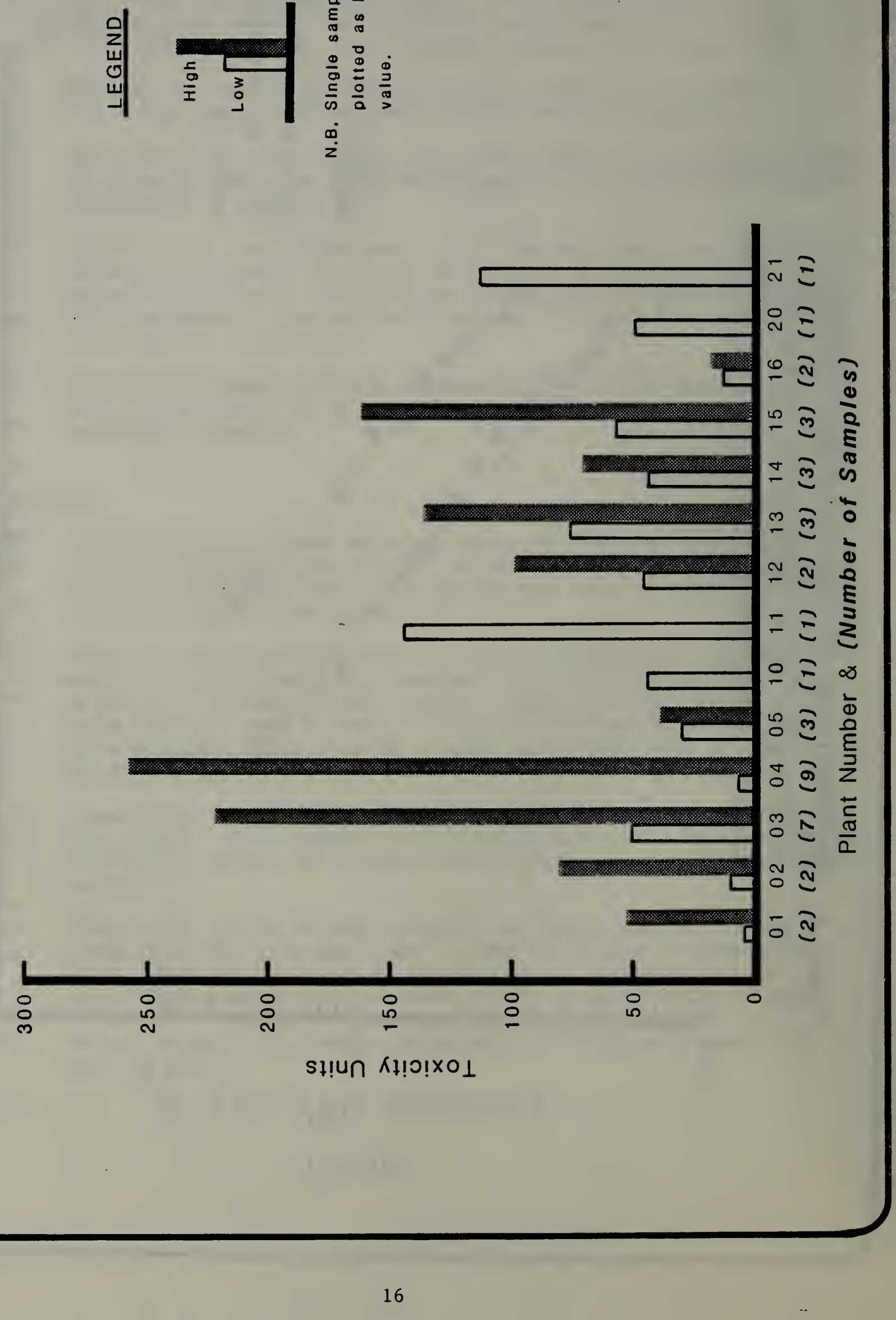
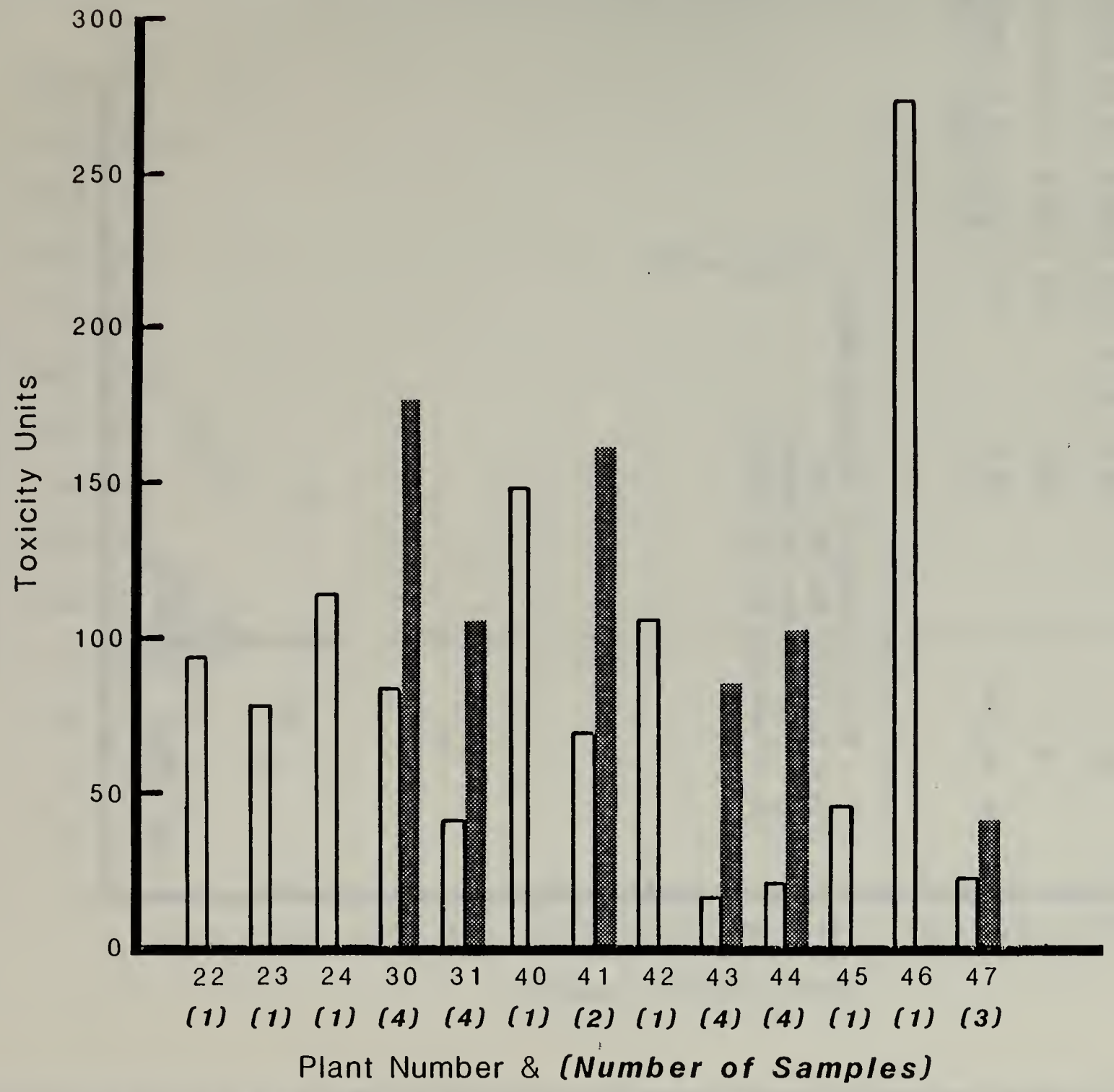
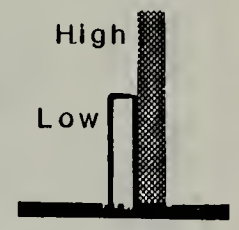


Figure 5b VARIATION IN EFFLUENT TOXICITY



LEGEND



N.B. Single sample plotted as low value.

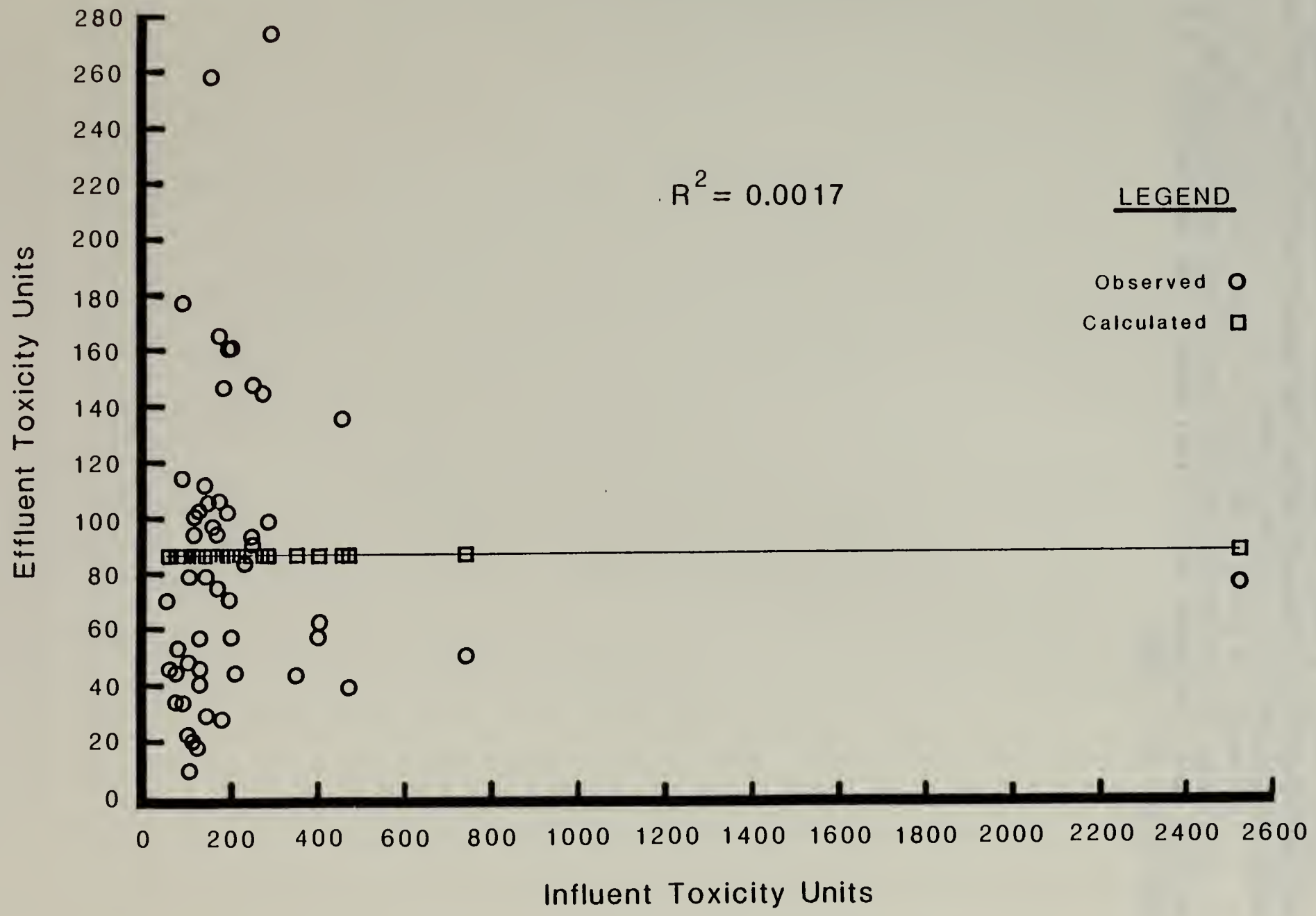
TABLE VI

CORRELATION BETWEEN SELECTED PARAMETERS AND TOTAL METAL TOXICITY OF MEASURED METAL

PARAMETER	R^2(%)	EQUATION*
Pb	47.3	$TT = 44.3 + 1.11\ (Pb_T)$
Hg	35.3	$TT = 62.6 + 1.21\ (Hg_T)$
Cu	23.7	$TT = 46.5 + 1.42\ (Cu_T)$
Pb, Hg, Cu	90.2	$TT = 13.2 + 1.03\ (Pb_T) + 1.04\ (Hg_T) + 0.995\ (Cu_T)$

TT = Total Toxicity of measured metals
Pb_T = Toxicity due to Lead
Hg_T = Toxicity due to Mercury
Cu_T = Toxicity due to Copper

Figure 6 CORRELATION BETWEEN INFLUENT AND EFFLUENT TOXICITY



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2. Burns and Roe Industrial Services Corp., Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, U.S. EPA, Washington, D.C., 1982.

Acknowledgments

The authors thank Dr. John Delaney, George Minasian and Kenneth Hume of the Lawrence Experiment Station for the chemical analyses. Aline L. Charest produced the manuscript and Robert J. Kerrigan created the graphics.

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